# Hg emissions to lake deposition: A qualitative analytical model and its application to Lake Whatcom, Washington

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The simple model described here was developed to be used primarily to evaluate in a consistent manner the possible atmospheric deposition of mercury (Hg) to lakes from past and present local sources of Hg. In the model, the three forms (species) of Hg (vaporous elemental, reactive gaseous, and particulate) initially emitted from a source are considered independently and the total deposition is the sum of the deposition of the three species. The reactivity of a species is characterized by its overall residence time in the atmosphere ($\tau_i$) once it has been discharged from the source. The general kinetic rate constant for removal of each specific species from the atmosphere is defined as

$$k_i = \ln(2) / \tau_i , \qquad (B1)$$

where $k_i$ is in units of the inverse of time ($T^{-1}$). The change in concentration of Hg for species $i$ in any parcel of air within an expanding plume is defined as

$$\partial C_{i,x,y,z} / \partial t = - k_i \bullet C_{i,x,y,z} , \qquad (B2)$$

where the concentration of Hg of species $i$ in the parcel of air ($C_{i,x,y,z}$) is in units of mass/length$^3$ (M L$^{-3}$), and $\partial C_{i,x,y,z} /\partial t$ is in units of (mass/length$^3$)/time or (M L$^{-3}$ T$^{-1}$). Because the change in the concentration of species $i$ ($-\partial C_{i,x,y,z}/\partial t$) is due to the removal of species $i$, the contribution of this parcel of air to the gain of Hg to the earth's surface (deposition) is simply $-k_i \bullet C_{i,x,y,z}$. The deposition rate of Hg species $i$ (Dep$_i$) to an area of land or water below (M L$^{-2}$ T$^{-1}$) is the integration of the Hg losses from all parcels of air over the height of plume ($dz$).

$$\text{Dep}_i = -\int \partial C_{i,x,y,z} /\partial t \, dz = k_i \int C_{i,x,y,z} \, dz . \qquad (B3)$$

In order to calculate the Hg concentration in the parcel of air once the plume has buoyantly risen and is traveling horizontally, the transport of Hg ($Q$ in units of M T$^{-1}$) through any plane perpendicular to the wind direction is

$$Q_i = u \iint C_{i,x,y,z} \, dy \, dz , \qquad (B4)$$

where $u$ is the wind speed in units of L T$^{-1}$ and $dy \, dz$ is the planar extent of the plume.

Because the change in the mass transport of Hg with time is simply the summation of losses of Hg over all the parcels of air in the plume that are moving past the plane perpendicular to the wind direction:

$$dQ_i / dt = -k_i Q_i . \qquad (B5)$$

Equation B5 can be transformed from time coordinates to space ($x$) coordinates by recognizing that $dt = dx/u$,

$$d Q_i /dx = -(k_i /u) Q_i , \qquad (B6)$$

whose analytical solution is

$$Q_{i,x} = Q_{i,0} e^{-k_i/u \bullet x} , \qquad (B7)$$

where $Q_{i,x}$ is the mass transport of species $i$ at distance $x$ in the direction of the wind field and $Q_{i,0}$ is the transport at source, which will be defined as the mass emission from the source.

The derivations up to this point are generalized for any plume behavior in a steady-state wind field. Plume dynamics in this model were simplified by assuming that (1) species $i$ is completely mixed across the plane of the plume at a given $x$, and (2) the lateral expansion of the plume is constant, forming a cone in the $xy$ plane with total angle of $\alpha$. The width of the plume ($y$) at any given $x$ is $2*\tan(\alpha/2) \bullet x$, which is approximated at small angles as $\tan(\alpha) \bullet x$. Equation B4 is then simplified to

$$Q_{i,x} = u \bullet \tan(\alpha) \bullet x \int C_{i,x} \, dz . \qquad (B8)$$

Substituting the mass flux at a given $x$ from equation B7 on the left side of equation B8, and substituting Dep$_i$ / $k_i$ (from equation B3) for $\int C_{i,x}, dz$ yields

$$Q_{i,0} e^{-k_i/u \bullet x} = u \bullet \tan(\alpha) \bullet \text{Dep}_i/k_i . \qquad (B9)$$

Solving equation B9 for deposition of species $i$ yields

$$\text{Dep}_i = k_i \bullet Q_{i,0} e^{-k_i/u \bullet x}/(u \bullet \tan(\alpha) \bullet x) . \qquad (B10)$$

Note that the deposition is independent of the thickness of the plume. Although expanding the thickness of the plume will decrease the concentration of species $i$ in the plume, deposition will occur over a longer air column ($dz$).

The simplifications of the plume dynamics allows one to use an analytical solution to estimate the deposition rate without having to numerically calculate the concentration of Hg species $i$ in the air mass. Given a specific wind field, deposition at a given point from the source was calculated knowing only the emission rate of species $i$ ($Q_{i,0}$) and its residence time ($\tau_i$). Equation B10 can be broken down into terms that are easily understandable. The $Q_{i,0}/u$ represents the dilution of the emission source by the wind field, much as the initial concentration of a pollutant in a river resulting from a point source discharge is dependent on the velocity of a river.

The term $e^{-k_i/u \bullet x}$ represents the decrease in the transport of the Hg species with distance from the source resulting from the deposition of species $i$ between the source and distance $x$. The term $1/(\tan(\alpha) \bullet x)$ represents the decrease in the concentration of species $i$ in the plume by the lateral dispersion of the plume with distance from the source. The decrease in concentration in the plume results in a decrease in the estimated deposition at a point under the plume.

If the plume was above the target receptor (target receptor direction is within wind direction $\pm \frac{1}{2}\alpha$), direct deposition of Hg to the site was calculated for that hour using equation B10 with the measured wind speeds, the distance from the source to the target receptor in miles, and a standard plume angle ($\alpha$) of 20 degrees. The hourly deposition amounts were summed over a year and the annual deposition was converted to SI units. Deposition for a unit emission of Hg ($Q_0 = 1$ g/hr) for residence times of 1 day, 1 week, 1 month, 1 quarter-year, and 1 year were calculated. The sensitivity of the model results was tested by

varying the plume angle ($\alpha$) from 5 to 20 degrees at a residence time of 1 week. This simplified model assumes steady-state conditions and assumes that a parcel of air will continue traveling in the recorded wind direction at the recorded wind speed even if it takes several hours to reach the receptor. This model probably is not valid during light and variable wind conditions (about 20 percent of the time), when a radially expanding plume model would be more appropriate.

An example of the model calculations for the three basins of Lake Whatcom, Washington for a hypothetical unit emission of Hg (1 g/hr) discharged in downtown Bellingham is given in figure B1. Because basin 1 of Lake Whatcom is in the direction of a primary wind pattern from Bellingham, deposition occurs 13 percent of the year at an $\alpha$ of 20 degrees, leading to the highest level of estimated deposition (fig. B1). Estimated deposition for a unit Hg emission decreases rapidly in the southerly direction down Lake Whatcom because the frequency of depositional events decreases to about 4 percent in basin 2 and less than 1 percent in basin 3. As with most source-receptor pairs, the model estimates of Hg deposition are insensitive to the value of the plume angle. As $\alpha$ decreases, the deposition per a

depositional event increases because the plume over the receptor is more concentrated, but the frequency of deposition events likewise decreases because of the narrowness of the plume.

The deposition rates to target lakes described above is for a unit emission of Hg with a specific half-life. Only after (1) the emission rate from a specific source is known or estimated, (2) the speciation among the three species, $i$, has been assessed, and (3) half-lives of each of the three species have been assigned to each species can the total deposition of Hg (TotDep) to the water surface be calculated as the sum of the depositions from three species:

$$\text{TotDep} = \text{Dep}_P + \text{Dep}_R + \text{Dep}_V, \qquad (B11)$$

where $\text{Dep}_P$ is the deposition of particulate mercury, $\text{Dep}_R$ is the deposition of reactive Hg, and $\text{Dep}_V$ is the deposition of vaporous mercury.

## Reference

Paulson, A.J., 2004, Sources of mercury in sediments, water, and fish of the lakes of Whatcom County, Washington: U.S. Geological Survey Scientific Investigations Report 2004-5084, 98 p. URL: http://pubs.water.usgs.gov/sir20045084.
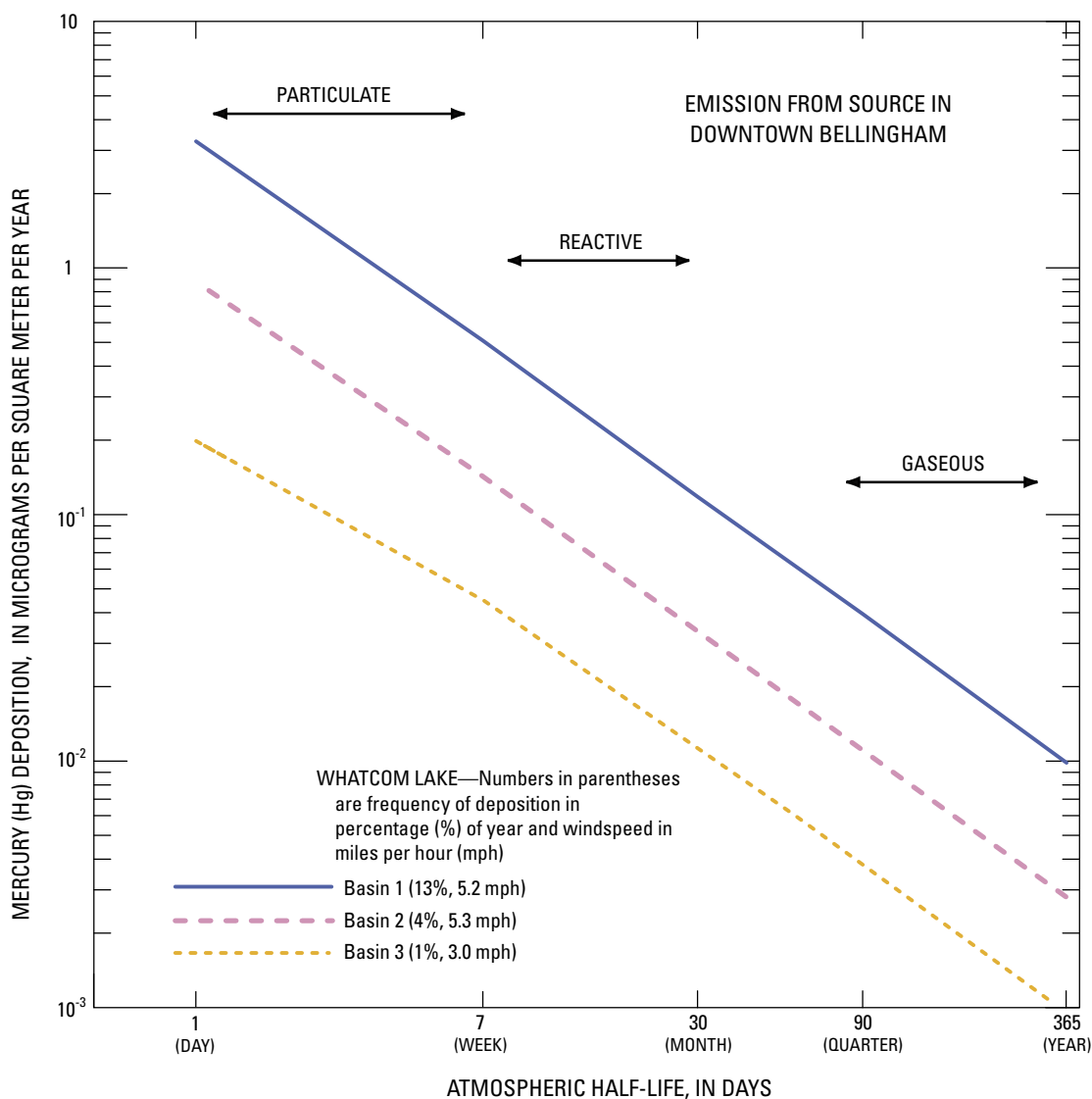
**Figure B1.** Deposition of mercury in Lake Whatcom from a hypothetical (1g/h) source in downtown Bellingham, Washington.